

Statistical and Low Temperature Physics (PHYS393)

## **2. Ideal Gas and Electron Gas**

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## Learning Aims: You will learn to

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State the formulae for average kinetic energy of atoms, total energy and heat capacity of the ideal gas.

State the quantisation condition for a particle in a cubic box. Explain and derive density of states for an ideal gas.

Explain why the ideal gas gives the wrong heat capacity for electrons in a metal.

State the formula for Fermi-Dirac distribution. Derive the formula for Fermi energy.

Derive the interval of energy from which electrons are excited. Derive the distribution of the excited electrons.

Derive the formula for heat capacity of electrons in a metal.

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## **Ideal Gas**

## A particle in a 3-D box

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In an ideal gas, we assume that there is little interaction between atoms. We shall learn how to calculate the total energy and other properties, and apply this to electrons, phonons, photons, liquid helium, etc.

From the kinetic theory of gases, we know that the average energy of each atom in an ideal gas is

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T.$$

This means that the total energy is

$$U = \frac{3}{2}Nk_B T$$

and the heat capacity is

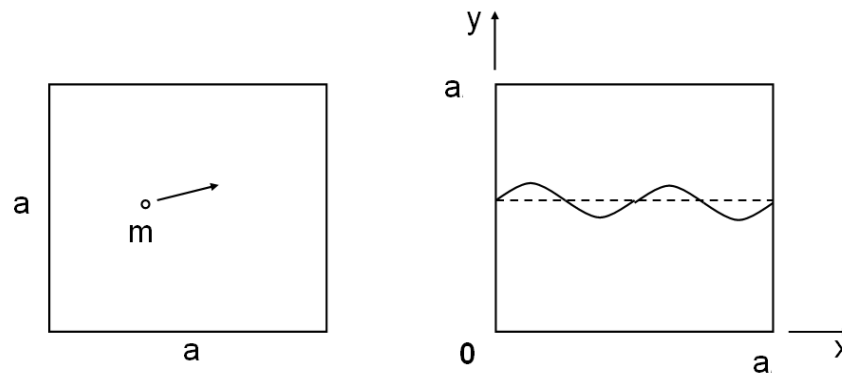
$$C = \frac{dU}{dT} = \frac{3}{2}Nk_B.$$

## Particle in a box

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Consider a particle in a 3-D box. One solution to the Schrodinger's equation is a wavefunction of the form

$$\psi(x) = \sin(k_x x).$$



The boundary condition that the wavefunction is zero at the edge of the box gives this quantisation condition in each direction:

$$k_x = \frac{n_x \pi}{a}.$$

where  $n_x$  is a positive integer. Likewise for the  $y$  and the  $z$ .

The other part of the solution to Schrodinger's equation is the energy of the wavefunction:

$$E = \frac{\hbar^2 k^2}{2m},$$

where  $m$  is the mass of the particle and  $k$  is the wavevector given by

$$k^2 = k_x^2 + k_y^2 + k_z^2.$$

We assume that in an ideal gas, each particle (atom, electron, ...) has the above quantisation condition and energy.

Then we can calculate the total energy of all particles, as well as many properties of the gas.

## Density of states.

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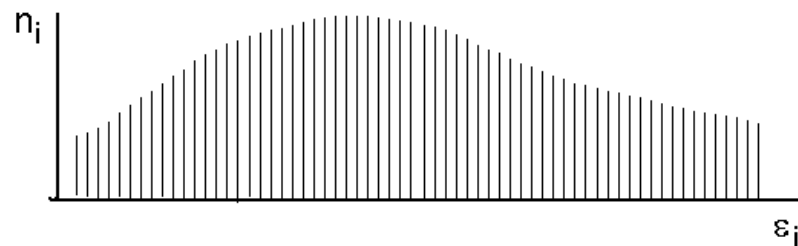
To find the total energy of  $N$  particles, we need to add up all their energies:

$$U = \sum n_i \varepsilon_i.$$

where  $\varepsilon_i$  is the energy of level  $i$  and  $n_i$  is the number of particles at that level.

At room temperature, many of these levels could be occupied. This is because for an ideal gas, spacing between energy levels is much smaller than the average energy of a particle.

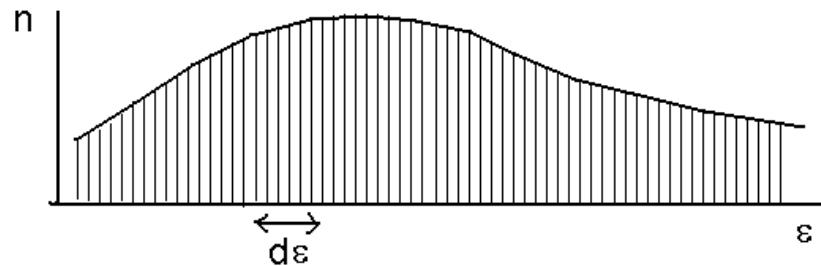
As a result, a plot of  $n_i$  against  $\varepsilon_i$  may look like this.



## Density of states.

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This suggests that we may approximate the graph to a curve, and the sum to an integral.



Within a small interval  $d\varepsilon$ , the energy  $\varepsilon$  is nearly constant. If we know the number of particles in this interval, we can multiply by  $\varepsilon$  to find the total.

Because of the quantisation condition, there can only be a certain number of states in  $d\varepsilon$ . For each state, there is a certain probability that it would be occupied. Lets start by find the number of states.



## Counting states

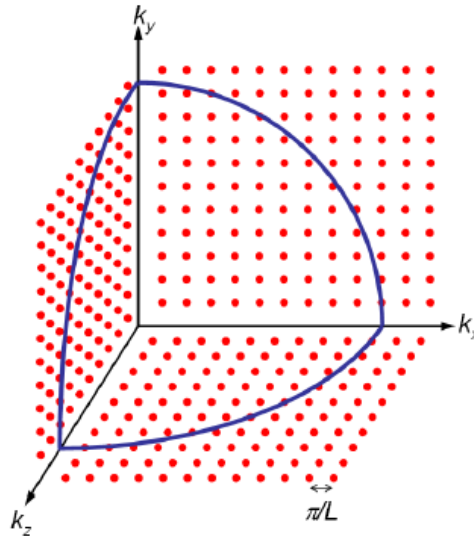
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The wavevectors

$$k_x = \frac{n_x \pi}{a}$$

are quantised at uniform intervals in all three directions.

we can imagine a  $k$  space in which the the  $x$  coordinate is  $k_x$ , and so on. If we use a point to represent each state, we would get a lattice like this.



## Counting states

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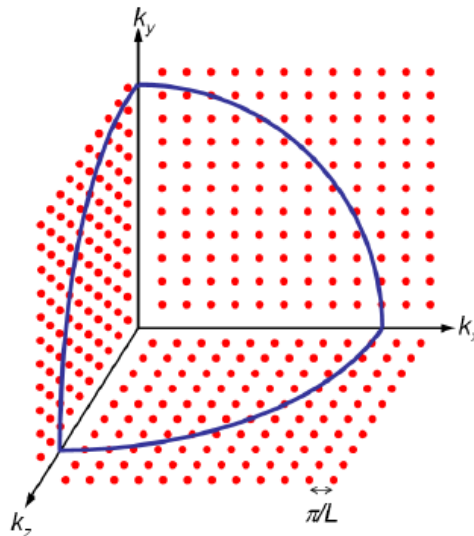
First, we find the number of all states below energy  $\varepsilon$ . This energy is related to the wavevector  $k$  by

$$\varepsilon = \frac{\hbar^2 k^2}{2m}.$$

$k$  is in turn related to the components by

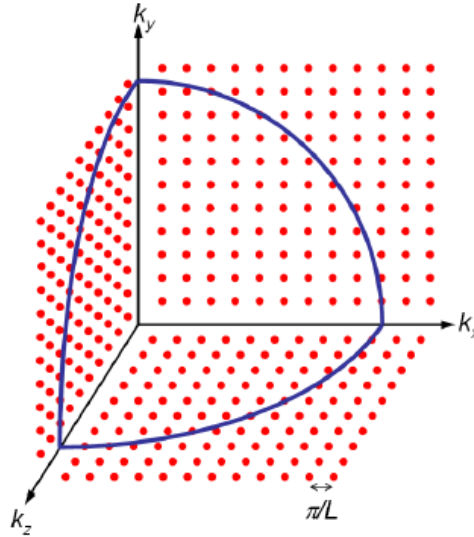
$$k^2 = k_x^2 + k_y^2 + k_z^2.$$

This describes a sphere in  $k$  space.



# DOS

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Because  $k_x$ ,  $k_y$  and  $k_z$  are all positive, only the points within 1/8 of the sphere of radius  $k$ , where  $k$  is the wavevector for  $\varepsilon$ .

Since the spacing between points is  $\pi/a$ , the volume associated with each point is  $(\pi/a)^3$ . Therefore, the total number of states is one eighth of the sphere volume divided by  $(\pi/a)^3$ :

$$G(k) = \frac{1}{8} \times \frac{4}{3}\pi k^3 \div \left(\frac{\pi}{a}\right)^3.$$

We find that the total number of states below  $k$  is

$$G(k) = \frac{V k^3}{6\pi^2},$$

where  $V$  is the volume  $a^3$  of the box.

Suppose  $k$  is increased by  $dk$ . Then the number of states increases by  $dG$ . So the density of states is

$$g(k) = \frac{dG(k)}{dk} = \frac{V k^2}{2\pi^2}.$$

We have earlier defined the DOS in terms of energy,  $\varepsilon$ .

To convert the variable from  $k$  to  $\varepsilon$ , we must use the method for probability density function:

$$g_\varepsilon(\varepsilon)d\varepsilon = g_k(k)dk.$$

The subscripts are added here to emphasise that  $g(\varepsilon)$  and  $g(k)$  are different functions.

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Rearranging,

$$g_{\varepsilon}(\varepsilon) = g_k(k) \frac{dk}{d\varepsilon}.$$

We can now substitute the relation

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

to find  $g_{\varepsilon}(\varepsilon)$ . The answer is

$$g(\varepsilon) = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}$$

where we have dropped the subscript again, as is the normal practice. For comparison:

$$g(k) = \frac{V k^2}{2\pi^2}.$$

If you substitute  $\varepsilon$  for  $k$  in  $g(k)$ , you DO NOT get  $g(\varepsilon)$ .  $g(k)$  and  $g(\varepsilon)$  are DIFFERENT functions!

It is also useful to have the formula for total number states

$$G(k) = \frac{1}{8} \times \frac{4}{3} \pi k^3 \div \left( \frac{\pi}{a} \right)^3.$$

in terms of energy.

Since no  $\varepsilon$  or  $k$  intervals are involved, we can simply substitute

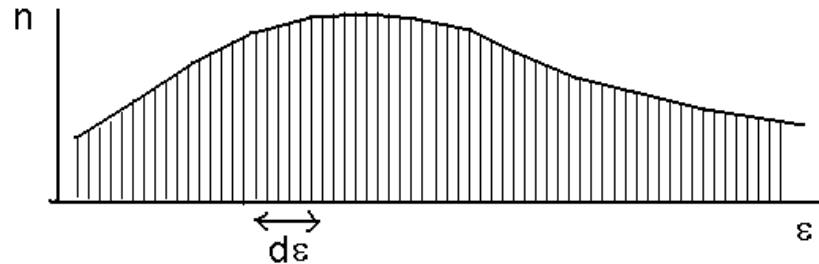
$$\varepsilon = \frac{\hbar^2 k^2}{2m}.$$

The answer is

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}.$$

## Probability that a state is occupied.

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The number of particles in an interval  $d\varepsilon$  is equal to the number of states in that interval times the probability that each state is occupied. From statistical mechanics, this probability is given by the Boltzmann distribution:

$$f(\varepsilon) = A \exp(-\varepsilon/k_B T).$$

where  $A$  is an unknown constant. So the number of states is

$$n(\varepsilon)d\varepsilon = A g(\varepsilon) \exp(-\varepsilon/k_B T) d\varepsilon,$$

where  $n(\varepsilon)$  is defined as the number of particles per unit energy, or the number density.

## Energy distribution.

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We can find  $A$  by summing to give

$$N = A \int_0^\infty g(\varepsilon) \exp(-\varepsilon/k_B T) d\varepsilon,$$

where  $N$  is the total number of particles. The integral

$$Z_{SP} = \int_0^\infty g(\varepsilon) \exp(-\varepsilon/k_B T) d\varepsilon.$$

is called the partition function. So we get  $A = N/Z_{SP}$ .

Substituting the formula for  $g(\varepsilon)$ , we find

$$A = \frac{N}{V} \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2}.$$

Substituting this into the formula for  $n(\varepsilon)$ , we finally get the full expression:

$$n(\varepsilon) = \frac{2\pi N}{(\pi k_B T)^{3/2}} (\varepsilon)^{1/2} \exp(-\varepsilon/k_B T).$$



## Total energy in ideal gas

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We can now find the total energy in an ideal gas. Replace the sum

$$U = \sum n_i \varepsilon_i$$

by the integral

$$U = \int_0^{\infty} n(\varepsilon) \varepsilon d\varepsilon.$$

Substitute the formula for number density:

$$U = \int_0^{\infty} \frac{2\pi N}{(\pi k_B T)^{3/2}} (\varepsilon)^{1/2} \exp(-\varepsilon/k_B T) \varepsilon d\varepsilon.$$

Integrating this gives the formula for the total energy that we know from kinetic theory of gases:

$$U = \frac{3}{2} N k_B T$$

This is evidence that the Boltzmann distribution for the ideal gas is correct.

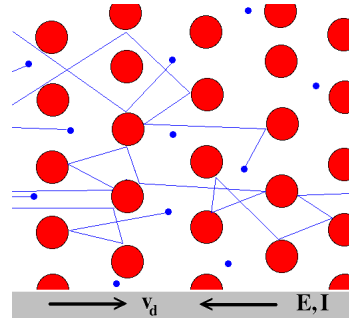
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## Fermi-Dirac statistics

## Electrons in a metal

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The Drude model was proposed in 1900 by Paul Drude to explain the transport properties of electrons in a metal.



This treats the electrons like an ideal gas. It explains very well the DC and AC conductivity in metals, the Hall effect, and thermal conductivity.

However, the ideal gas formula

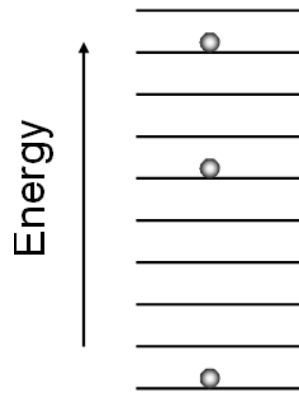
$$C = \frac{3}{2} N k_B$$

greatly overestimates the heat capacities of electrons in a metal.

## Why did the electron gas model fail?

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The Boltzmann distribution for the ideal gas has an assumption: that it is unlikely for two atoms to occupy the same energy level.



This is valid for an ideal gas at room temperature, because the energy levels are very close together, compared to the average energy of the atoms.

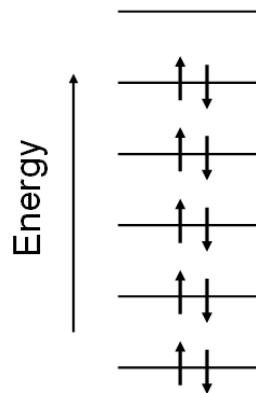
Unfortunately, this is no longer true for electrons in a metal.

## The exclusion principle

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Because of the electrons are much lighter, the energy spacings are also much wider. So it is quite likely that two electron would occupy the same state at lower energy.

However, electrons are not allowed to occupy the same energy states. So they have to be stacked up from bottom to top.



When heated, most of the electrons are stuck - there is no space above to move up in energy !

Only those near the very top can. So the heat capacities are much smaller than that of an ideal gas.

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For these reasons, we cannot use the Boltzmann distribution for the ideal gas.

Instead, we need to use the Fermi-Dirac distribution:

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{\exp((\varepsilon - \mu)/k_B T) + 1}.$$

where  $\mu$  is an unknown constant, called chemical potential.

The total number of electrons is fixed and is given by integrating the normalisation condition:

$$N = \int_0^\infty \frac{g(\varepsilon)d\varepsilon}{\exp((\varepsilon - \mu)/k_B T) + 1}$$

In principle, we could solve for  $\mu$ . In practice, this is usually difficult.

## Occupying the energy states

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For convenience, we define the following function:

$$f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)} = \frac{1}{\exp((- \mu + \varepsilon)/k_B T) + 1}$$

This is the probability that a state is occupied.

$f(\varepsilon)$  is also called the occupation number. We need to see what this looks like and how it changes with temperature.

Lets start with the simplest case:  $T = 0$  K. If we allow  $T$  to approach zero, we find:

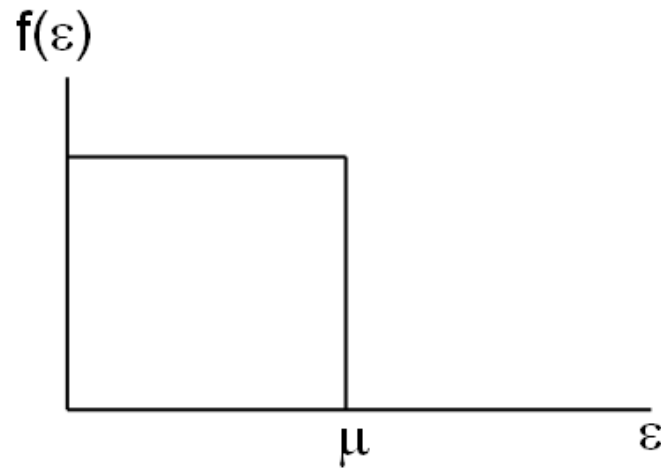
$$\begin{aligned} f(\varepsilon) &= 1 \text{ for } \varepsilon < \mu \\ f(\varepsilon) &= 0 \text{ for } \varepsilon > \mu \end{aligned}$$

This means that all states with energy below  $\mu$  are fully occupied. All states with energy above  $\mu$  are empty.

## Occupying the energy states

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The graph for  $f(\varepsilon)$  looks like this



The shape shows that the energy levels are occupied below a certain energy, and unoccupied above that.

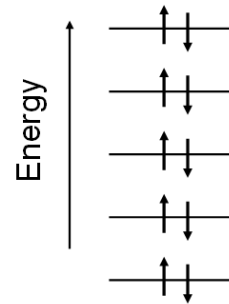
This feature is characteristic of the Fermi-Dirac distribution that we are studying.



## The Fermi energy

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At  $T = 0\text{K}$ , The highest energy in the stack of electrons is  $\mu$ . This energy is also called the Fermi energy,  $E_F$ .



We can find the Fermi energy  $E_F$  by integrating the normalisation condition:

$$N = 2 \times \int_0^\infty n(\varepsilon) d\varepsilon$$

The factor of 2 must be added because each energy state can be occupied by 2 electrons - spin up and spin down.

We shall solve this for the Fermi energy  $E_F$ .

## The Fermi energy

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In terms of the occupation number,

$$n(\varepsilon) = g(\varepsilon)f(\varepsilon)$$

So the normalisation condition can be written as:

$$N = 2 \times \int_0^\infty n(\varepsilon)d\varepsilon = 2 \times \int_0^\infty g(\varepsilon)f(\varepsilon)d\varepsilon$$

We know that at 0K,  $f(\varepsilon) = 0$  for  $\varepsilon > \mu$ . So the integration would stop at  $\varepsilon = \mu$ :

$$N = 2 \times \int_0^{E_F} g(\varepsilon)f(\varepsilon)d\varepsilon$$

since  $\mu = E_F$  at 0K.

We also know that at 0K,  $f(\varepsilon) = 1$  for  $\varepsilon < \mu$ . So

$$N = 2 \times \int_0^{E_F} g(\varepsilon)d\varepsilon$$

## The Fermi energy

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We have previously derived the density of states:

$$g(\varepsilon) = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}$$

In the topic on ideal gas, this is obtained by counting the number of energy states of a particle in a 3-D box. In this topic on electrons, we have used the same particle in a box model.

So the same formula for the density of states can be used for both the ideal gas and the electrons. We can therefore substitute the formula into the normalisation integral

$$N = 2 \times \int_0^{E_F} g(\varepsilon) d\varepsilon$$

and solve for the Fermi energy. The result is

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.$$

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## Electronic heat capacity

We want to use the ideas and formulae that we have developed to calculate the heat capacity of electrons.

To see how to do this, recall that the Drude model would predict for electrons a heat capacity that is the same as that of an ideal gas:

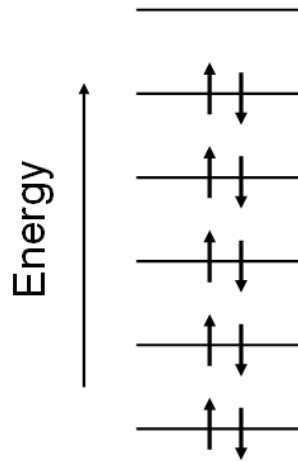
$$C = \frac{3}{2}Nk_B.$$

It is known from experiments that the actual heat capacity of the electrons is much smaller.

## Heat capacity

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We can understand this if we think that the electrons that are stacked up to the Fermi energy do not have enough energy to jump out of the stack.



This would only be true if the thermal energy is much smaller than the Fermi energy.

Lets find out if this is true.

## Heat capacity

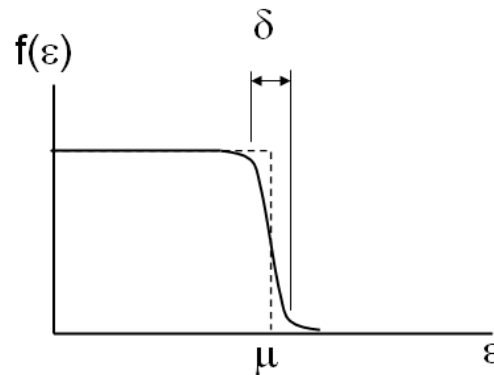
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Assume that the thermal energy is indeed much smaller than the Fermi energy. We shall derive an expression for this thermal energy, and then calculate it at room temperature to see if the assumption can be justified.

At a temperature above 0 K, the occupation number

$$f(\varepsilon) = \frac{1}{\exp((- \mu + \varepsilon)/k_B T) + 1}$$

no longer has a sharp step at the Fermi energy.

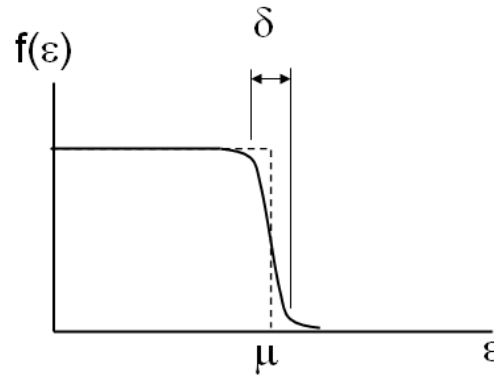


If  $k_B T$  is much smaller than  $\mu$ , the graph would remain close to the step.

## Heat capacity

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The "smoothened" slope of the graph tells us that electrons just below the Fermi energy ( $\mu = E_F$ ) is excited above it.



We can estimate the gain in thermal energy of the excited electrons from the width  $\delta$  of this slope.

Lets take a closer look at the occupation number

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}$$



## Heat capacity

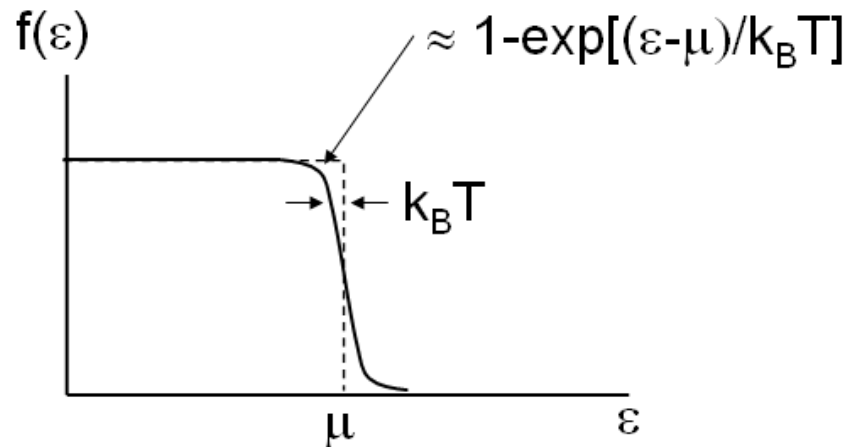
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For energy  $\varepsilon$  lower than  $\mu$  by a few times of  $k_B T$ , The exponential function  $\exp[(\varepsilon - \mu)/k_B T]$  would quickly become small.

The occupation number is then approximately

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1} \rightarrow 1 - \exp[(\varepsilon - \mu)/k_B T]$$

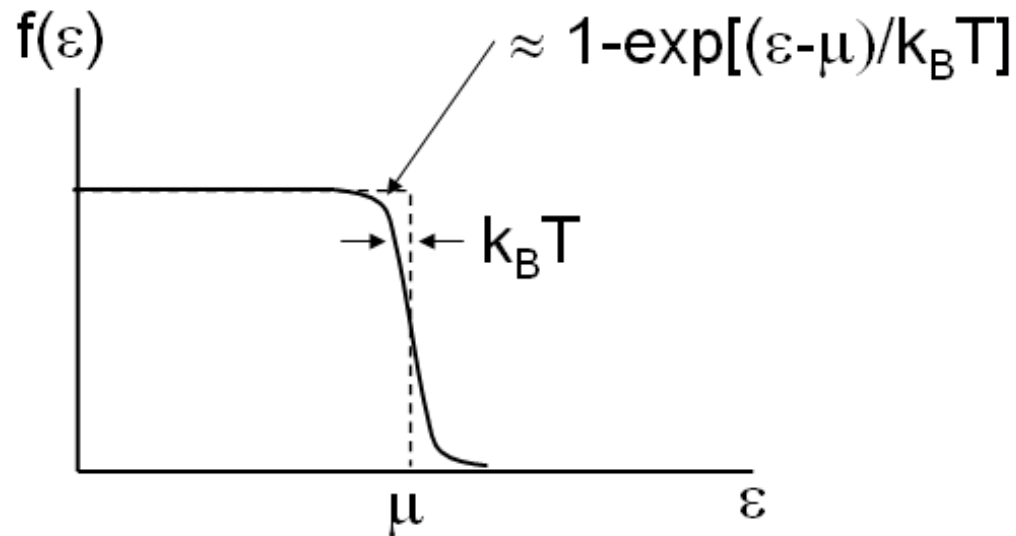
where we have used the binomial expansion and kept only the first order term.



## Heat capacity

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This means that the part of the graph to the left of  $\mu$  tends to the line  $f(\varepsilon) = 1$  exponentially.



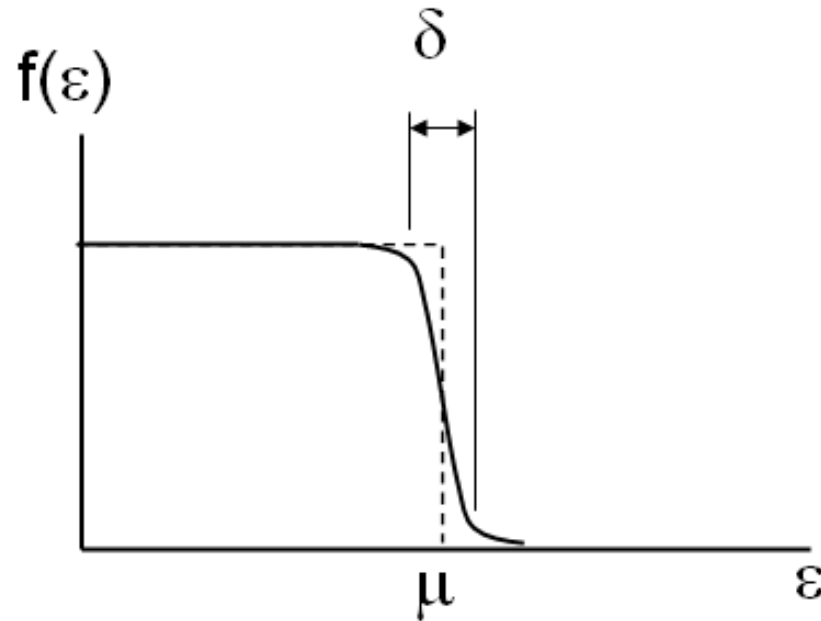
It reaches within  $f(\varepsilon) = 1$  by a fraction of  $1/e$ , over an energy range of  $k_B T$ .

This means that it is the electrons within this energy range that is excited. So the thermal energy of the excited electrons is of the order of  $k_B T$ .

## Heat capacity

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When temperature increases above 0 K, the step in the Fermi-Dirac distribution becomes smoother as electrons just below the Fermi energy are excited above it.



Notice that the "tail end" of the distribution - to the right - looks exponential. Maybe, these electrons can behave like the ideal gas and approximately obey the Boltzmann distribution.

Lets find out.

## Heat capacity

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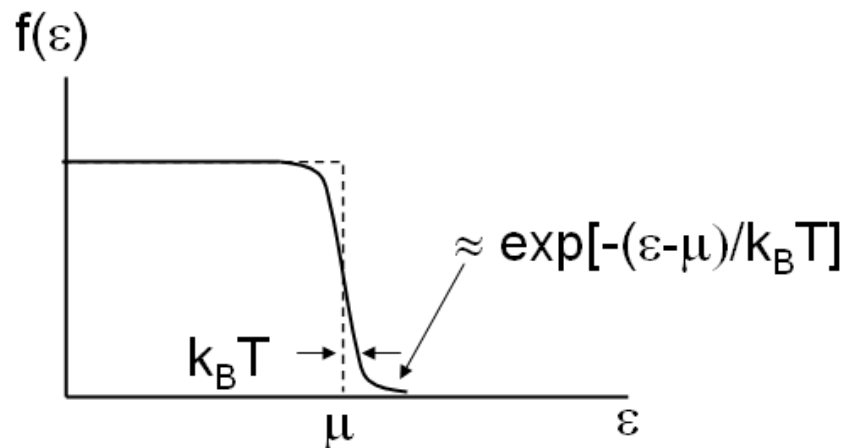
For energy  $\varepsilon$  higher than  $\mu$  by a few times of  $k_B T$ , The exponential function  $\exp[(\varepsilon - \mu)/k_B T]$  would quickly become large.

Then

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1} \rightarrow \frac{1}{\exp[(\varepsilon - \mu)/k_B T]}$$

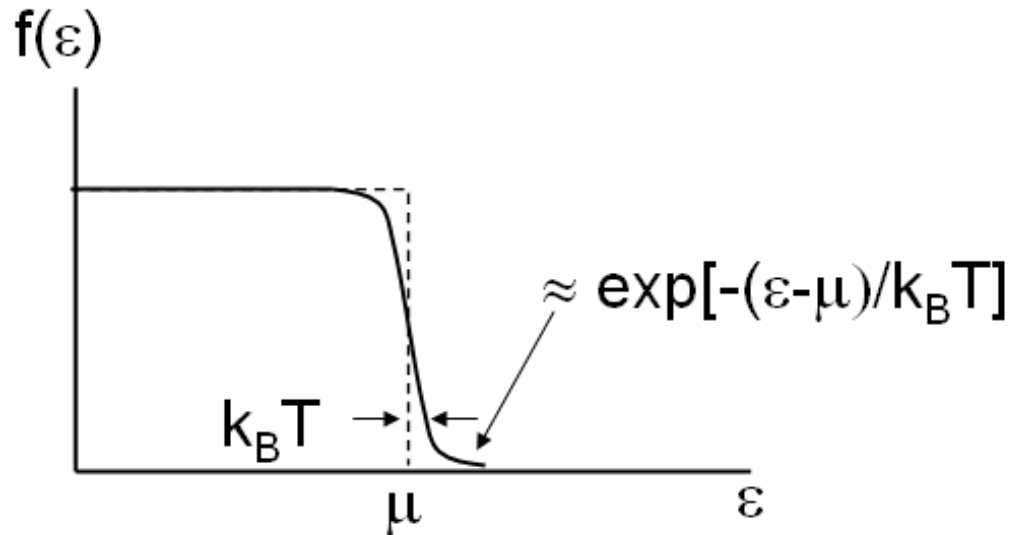
which is just the exponential function with negative argument

$$f(\varepsilon) = \exp[-(\varepsilon - \mu)/k_B T].$$



This means that the part of the graph to the right of  $\mu$  falls off exponentially.

The excited electrons follow a Boltzmann distribution!



Note also that the graph falls by a fraction of  $1/e$  over an energy range of  $k_B T$ .

At this point, we should justify our assumption that  $k_B T$  at room temperature is much smaller than the Fermi energy  $\mu = E_F$ , which is defined at 0 K.

We shall take sodium metal as an example, and calculate  $k_B T$  and  $E_F$  for this metal.

In sodium, each atom has one valence electron. This electron is mobile and forms the electron gas that we are talking about. In order to calculate the Fermi energy, we need the number density  $N/V$ . We can calculate this from the following data:

$$\text{density} = 0.97 \text{ g cm}^{-3}$$

$$\text{relative atomic mass} = 23.0$$

So the volume for one mole of atoms is

$$23 \div 0.97 = 23.71 \text{ cm}^3,$$

and the number density is

$$\frac{N}{V} = N_A \div 23.71$$

where  $N_A$  is Avogadro's number. This gives an answer of  $2.54 \times 10^{28} \text{ m}^{-3}$ .

Using the Fermi energy formula,

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.$$

where  $m$  is the mass of the electron, we can find that the Fermi energy is 3.16 eV.

In contrast, at room temperature 298 K, we can calculate that

$$k_B T \approx \frac{1}{40} \text{eV}.$$

This is about 120 times smaller than the Fermi energy.

We can repeat this for other typical metals, and we would get similar answers.

This justifies our assumption that at room temperature  $k_B T$  is much smaller than the Fermi energy.

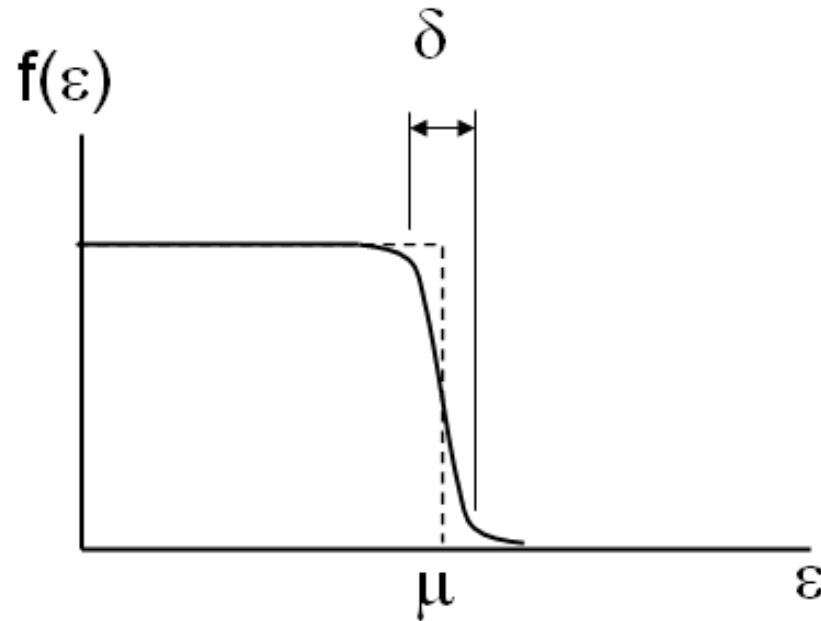
We are now a step closer to estimating the electronic heat capacity. Next, we need to understand the behaviour of the excited electrons.



## Heat capacity

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It is clear now that at room temperature, only electrons close to the Fermi energy are excited. Most of the electrons are below the Fermi energy and are not excited at all. Since they cannot be excited, these electrons would not contribute to the heat capacity .



So it is mainly electrons close to Fermi energy that would contribute to the heat capacity. We can use these to estimate the heat capacity and ignore the rest.

As we have seen, excited electrons behave like the ideal gas. We know that the energy of ideal gas is

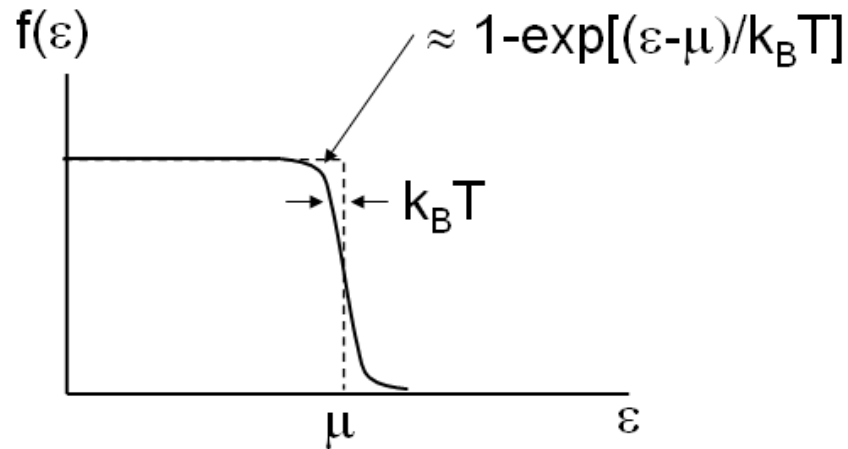
$$U_1 = \frac{3}{2}N_1k_BT$$

where  $N_1$  is the number of particles in the ideal gas.

In the case of the electrons in metal,  $N_1$  refers to the number of electrons above the Fermi energy, and not the total number of electrons. We can estimate this number as follows.

## Heat capacity

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We know that the number of particles in a given energy interval is

$$n(\epsilon)d\epsilon = 2g(\epsilon)f(\epsilon)d\epsilon$$

where the factor of 2 again comes from the spin states of the electrons.

At 0 K, the energy states below  $E_F$  are fully occupied, i.e.  $f(\epsilon) = 1$ . At temperature  $T$ , the number would be

$$N_1 \approx 2g(E_F)k_B T$$

## Heat capacity

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From the definitions of the density of state and the Fermi energy, it can be shown that

$$g(E_F) = \frac{3N}{4E_F}$$

where  $N$  is the total number of electrons. This gives

$$N_1 \approx 2 \left( \frac{3N}{4E_F} \right) k_B T = \frac{3}{2} N \frac{k_B T}{E_F}$$

Substituting into the energy for ideal gas

$$U_1 = \frac{3}{2} N_1 k_B T$$

we get the energy for the excited electrons

$$U_1 = \frac{3}{2} \left( \frac{3}{2} N \frac{k_B T}{E_F} \right) k_B T = \frac{9}{4} N k_B \frac{k_B T^2}{E_F}$$

Differentiating with respect to  $T$ , we get the electronic heat capacity

$$C = \frac{9}{2} N k_B \frac{k_B T}{E_F}$$

## Heat capacity of a metal

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We have obtained the electronic heat capacity

$$C = \frac{9}{2} N k_B \frac{k_B T}{E_F}$$

More detailed calculations show that the factor of  $9/2$  should really be  $\pi^2/2$ :

$$C = \frac{\pi^2}{2} N k_B \frac{k_B T}{E_F}$$

For 1 mole of electrons,  $N = N_A$ , and the equation can be written as

$$C = \frac{\pi^2}{2} R \frac{T}{T_F}$$

where  $T_F = E_F/k_B$  is called the Fermi temperature.

## Heat capacity of a metal

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Notice that the heat capacity is directly proportional to  $T$ .

$$C = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

This is often written in the form

$$C = \gamma T.$$

There is another contribution to heat capacity of metal. This comes from the vibrations of the atoms, and it is proportional to  $T^3$ .

We could imagine writing the total heat capacity in the form:

$$c_V = \gamma T + AT^3.$$

We can measure this heat capacity to check if the formula is correct. Suppose that we have obtained a table of values for  $T$  and  $c_V$ . To check if the formula is correct, we can rewrite it in this form:

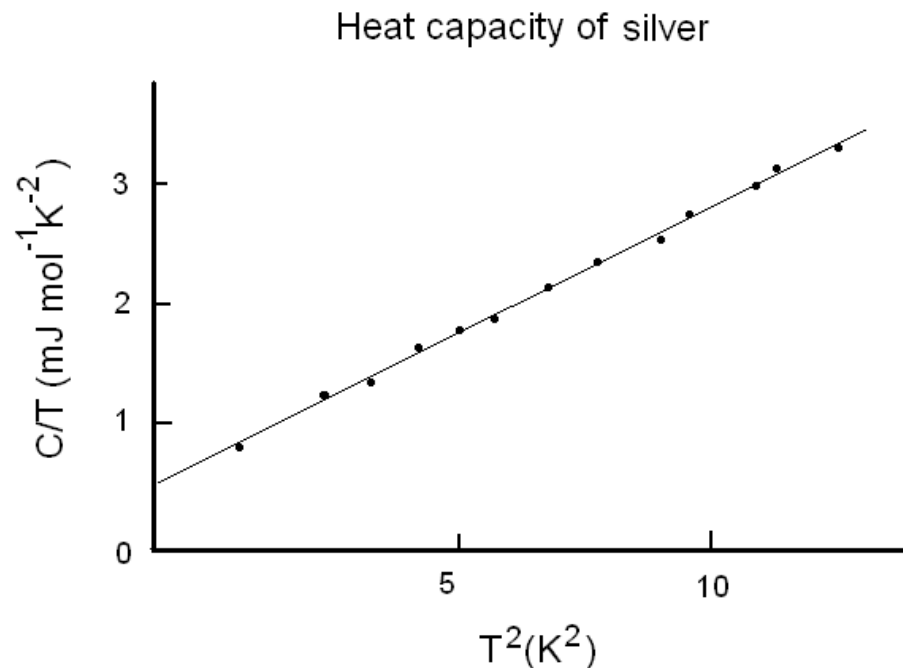
$$c_V/T = \gamma + AT^2$$

## Heat capacity of a metal

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In 1955, William Corak and his fellow co-workers measured the heat capacities of copper, gold and silver from 1K to 5K in their laboratory in Pittsburgh.

They plotted  $c_V/T$  against  $T^2$ , and got the straight lines. The picture here is a sketch of their results. This shows that the predictions of the Fermi-Dirac statistics are correct.



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## Worked Examples



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## Example 1

A bottle contains 2 moles of neon gas at 20 °C.

(i) Write down the formula for average kinetic energy of particles in an ideal gas. What is the average kinetic energy of the neon atoms?

(ii) Write down the formula for total number of states. What is the total number of states below this energy? Assume that volume of the gas is  $23.8 \text{ dm}^{-3}$ , and relative atomic mass of neon is 20.

(iii) Write down the formula for density of states. What is the density of states at this energy?

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## Solutions

(i) Formula for average kinetic energy of particles in an ideal gas is

$$\varepsilon = \frac{3}{2}k_B T.$$

where  $T$  is the temperature.

Temperature  $T = 273 + 20 = 293$  K. Average kinetic energy of the neon atoms is

$$\varepsilon = \frac{3}{2} \times 1.38 \times 10^{-23} \times 293 = 6.065 \times 10^{-21} \text{ J}.$$

(ii) Formula for total number of state:

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}.$$

Volume  $V = 23.8 \text{ dm}^{-3} = 23.8 \times 10^{-3} \text{ m}^{-3}$ .

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Mass of neon atom  $= 20m_u = 20 \times 1.66 \times 10^{-27}$  kg.

Substituting, we find that total number of states below  $\varepsilon$  is

$$G(\varepsilon) = 2.765 \times 10^{30}.$$

(iii) Formula for density of states is

$$g(\varepsilon) = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}$$

Substituting, we find that density of states at  $\varepsilon$  is

$$g(\varepsilon) = 6.837 \times 10^{50} \text{ J}^{-1}.$$

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## Example 2

A piece of copper contains one mole of atoms. Each atom gives one conduction electron.

Suppose that these electrons form an ideal gas.

- (i) Find the total energy of these electrons at 300 K.
- (ii) Find the average kinetic energies of the electrons.
- (iii) Find the heat capacity of the electrons.

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## Solutions

(i) Formula for total energy of one mole of ideal gas is

$$U = \frac{3}{2}RT.$$

where  $T$  is temperature. Given  $T = 300$  K. So

$$U = \frac{3}{2} \times 8.31 \times 300 = 3739.5 \text{ J.}$$

(ii) Formula for average kinetic energy of particles in an ideal gas is

$$\varepsilon = \frac{3}{2}k_B T.$$

where  $T$  is the temperature.

Average kinetic energy of the electrons is

$$\varepsilon = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.210 \times 10^{-21} \text{ J.}$$

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(iii) Heat capacity of the electrons is

$$C = \frac{3}{2}R = \frac{3}{2} \times 8.31 = 12.47 \text{ J/K.}$$

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### Example 3

In fact, only the excited electrons in copper behave like an ideal gas.

(i) Write down the correct formula for the heat capacity of the electrons in terms of the Fermi energy.

(ii) The volume for one mole of copper is  $7.11 \text{ cm}^3$ . Each copper atom gives one conduction electron. Find the Fermi energy.

(iii) Find the correct heat capacity of the copper at 300 K. What percentage is this compared to the ideal gas result in Example 2?

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## Solutions

(i) The correct formula for heat capacity of the electrons is

$$C = \frac{9}{2} N k_B \frac{k_B T}{E_F}.$$

(ii) Fermi energy is

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.$$

$$m = m_e$$

$$N = N_A$$

$$V = 7.11 \text{ cm}^3 = 7.11 \text{ m}^6.$$

Substituting, we find

$$E_F = 1.117 \times 10^{-18} \text{ J}.$$



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(iii) Substituting the above values, the correct heat capacity of the copper is

$$C = \frac{9}{2} N k_B \frac{k_B T}{E_F} = 0.1386 \text{ J/K.}$$

Compared with the ideal gas calculation, this is

$$0.1386/12.47 \times 100 = 1.112\%.$$

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## Example 4

- (i) Write down the formula for total number of states,  $G(\varepsilon)$ , below energy  $\varepsilon$  for particles in an ideal gas.
- (ii) Derive the Fermi energy formula using  $G(\varepsilon)$ .
- (iii) Derive  $g(E_F)$  in terms of  $E_F$  and number of particles  $N$  only (without  $V$ ,  $m$  or  $h$ ).

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## Solutions

(i) Formula for total number of states:

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}.$$

(ii) Two electrons can occupy each energy state. So total number of electrons states below the energy  $\varepsilon$  is  $2G(\varepsilon)$ .

At 0 K, all electrons are below  $E_F$ , so total number of electrons is:

$$N = 2G(E_F).$$

Substituting the total number of states formula:

$$N = 2 \times \frac{4\pi V}{3h^3} (2mE_F)^{3/2}.$$

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Rearranging:

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.$$

(iii) Notice that the total number of states may be written in this form:

$$G(\varepsilon) = K\varepsilon^{3/2}.$$

where  $K$  is a factor that does not depend on  $\varepsilon$ .

Taking log on both sides and differentiating with respect to  $\varepsilon$ , we find the density of states

$$g(\varepsilon) = \frac{3}{2}K\varepsilon^{1/2}.$$

Dividing this by the previous equation, we eliminate  $K$ :

$$\frac{g(\varepsilon)}{G(\varepsilon)} = \frac{3}{2\varepsilon}.$$

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At Fermi level,  $\varepsilon$  is  $E_F$ :

$$\frac{g(E_F)}{G(E_F)} = \frac{3}{2E_F}.$$

Since  $G(E_F)$  is the total number of states below Fermi level, so the total number of electrons is

$$N = 2G(E_F).$$

Substituting this into the previous equation and rearranging, we get

$$g(E_F) = \frac{3N}{4E_F}.$$

## Learning Outcome: You should be able to

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State the formulae for average kinetic energy of atoms in an ideal gas, the total energy and heat capacity of the ideal gas.

State the quantisation condition for a particle in a cubic box. Explain and derive density of states for an ideal gas.

Explain why the ideal gas gives the wrong heat capacity for electrons in a metal.

State the formula for Fermi-Dirac distribution. Derive the formula for Fermi energy.

Derive the interval of energy from which electrons are excited. Derive the distribution of the excited electrons.

Derive the formula for heat capacity of electrons in a metal.